

The oxidation behaviour of mixed tungsten silicon sputtered coatings

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Abstract

W–Si–N coatings were deposited by sputtering and their chemical composition, structure, thermal and oxidation behaviour were characterised. Si-containing films are essentially amorphous. $W_{69}Si_{31}$ film crystallises at 750°C as α -W and W_5Si_3 phases whereas no significant structural transformations were observed for $W_{24}Si_{12}N_{55}$ film up to 1000°C. In both cases elemental diffusion (Si and N) for the substrate was detected after thermal annealing. These coatings present much better oxidation resistance than W and $W_{15}N_{85}$ coatings. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Owing to the excellent mechanical properties of bulk tungsten compounds, extensive research work has been carried out in the last decade to deposit W-based materials under the form of thin coatings, particularly by PVD techniques.

In previous research work [1], we demonstrated that W and W–N coatings suffer extensive oxidation degradation for temperatures higher than 700°C. Moreover, it was possible to conclude that the addition of Ti or Ni to W–N coatings could increase their oxidation resistance, for the same degree of degradation, at temperatures some tens of °C higher.

The addition of silicon has a beneficial role on the oxidation behaviour of materials. For example, Hirvonen et al. [2] demonstrated that amorphous Mo–Si coatings deposited by sputtering resist up to 1000°C in oxidant environments. However, this resistance was only observed for the films containing nitrogen.

Thus the objective of this research work was:

- to deposit W-based coatings by sputtering with and without Si and N,
- to characterise the coatings concerning their structure, chemical composition and thermal behaviour,
- to evaluate and to try to understand the role of Si and N on the oxidation resistance of the films.

2. Experimental details

2.1. Deposition technique

The films were deposited by DC reactive magnetron sputtering with a specific target power density of 10 W/cm² and a negative substrate bias of 70 V. The target is pure W (150 × 150 mm); for the deposition of W–Si films round pieces of pure silicon (1 mm thick) were glued on the target. When the reactive mode was used the N₂/Ar partial pressure ratio was 2/1 and 1/1 for W–N and W–Si–N films, respectively, for a total deposition pressure of 0.3 Pa. The substrates of steel (318 - AISI) were polished on both faces with diamond paste down to a particle size of 1 µm. Before deposition, the sputtering chamber was evacuated by a turbomolecular pump down to a final pressure of 10^{−4} Pa. The substrate surfaces were then ion cleaned by an ion gun.

2.2. Characterisation techniques

Thermogravimetric tests were carried out on a Polymer Science thermobalance of high resolution (0.1 µg). Oxidation temperatures ranged from 600–1000°C. The samples were heated up to the oxidation temperature at a fixed heating rate of 30°C min^{−1}. A constant isothermal time of 30 min was used. Industrial air of 99.995% purity was used as oxidant gas.

The structure of the films was analysed by X-ray diffraction (XRD) using a Siemens diffractometer with Cu–K_α radiation. This equipment was provided with a furnace allowing the samples to be heated up to 1200°C. Thermal annealing of the films was carried out in a vacuum with

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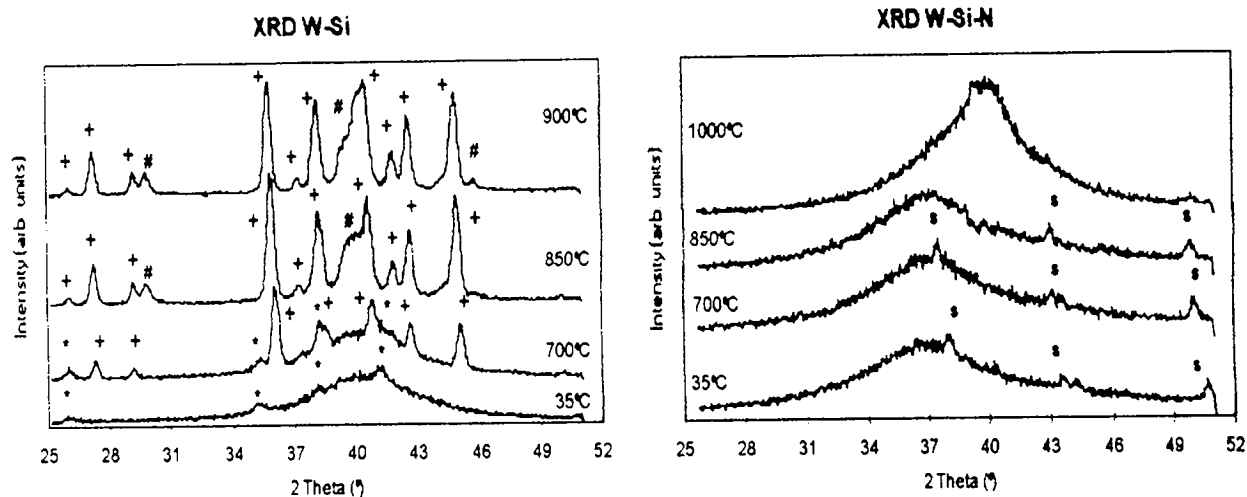


Fig. 1. In situ XRD diffractograms of W-Si and W-Si-N sputtered films taken at increasing annealing temperatures (only the diffractogram's greatest characteristics are shown), s, substrate; *, WSi_2 hexagonal; +, W_5Si_3 ; #, WSi_2 tetragonal.

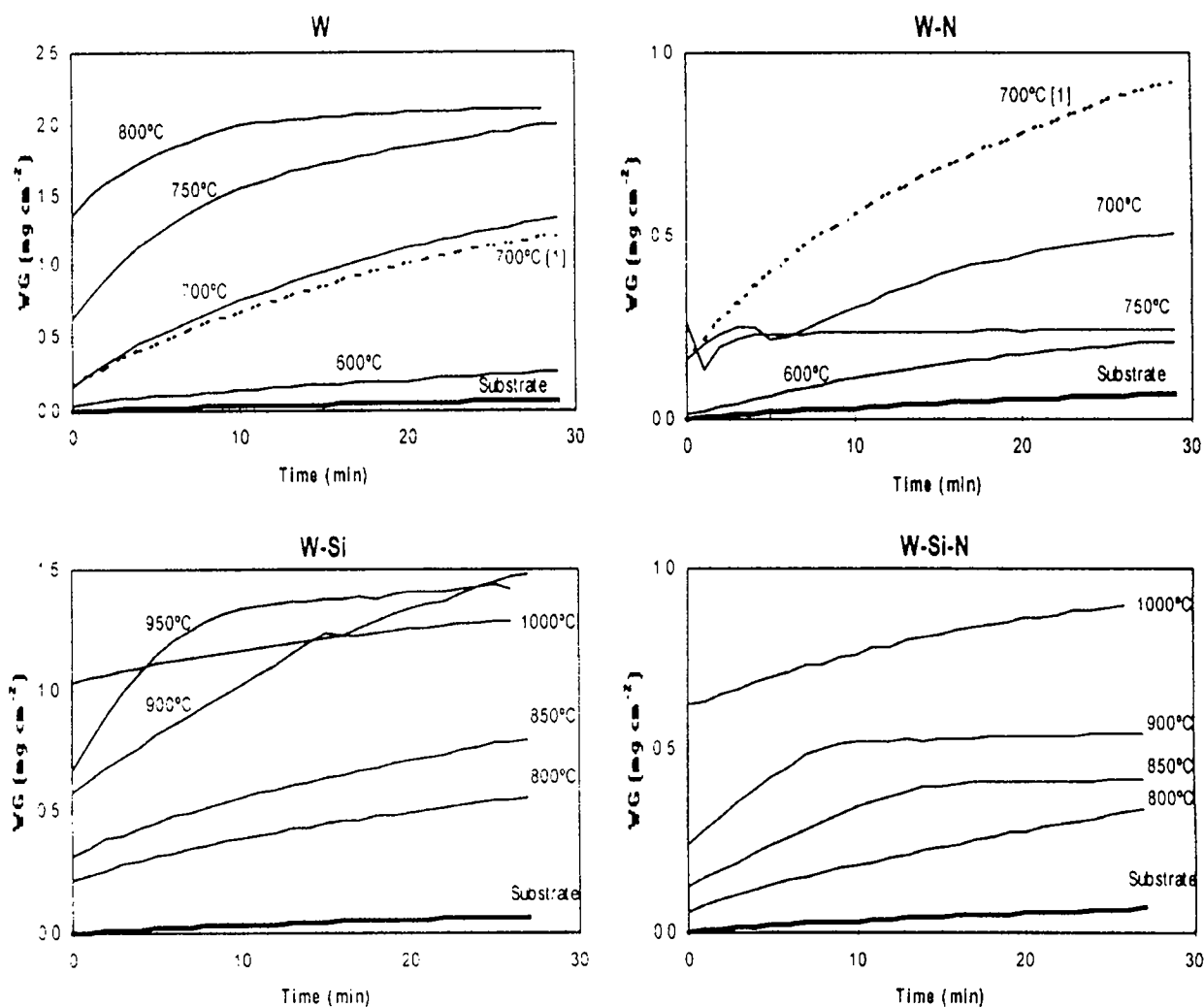


Fig. 2. Isothermal oxidation curves of W, W-N, W-Si and W-Si-N films. The curve for the substrate oxidised at 1000°C, as well as the curves for W and W-N films oxidised at 700°C and characterised in previous work [1], is also shown.

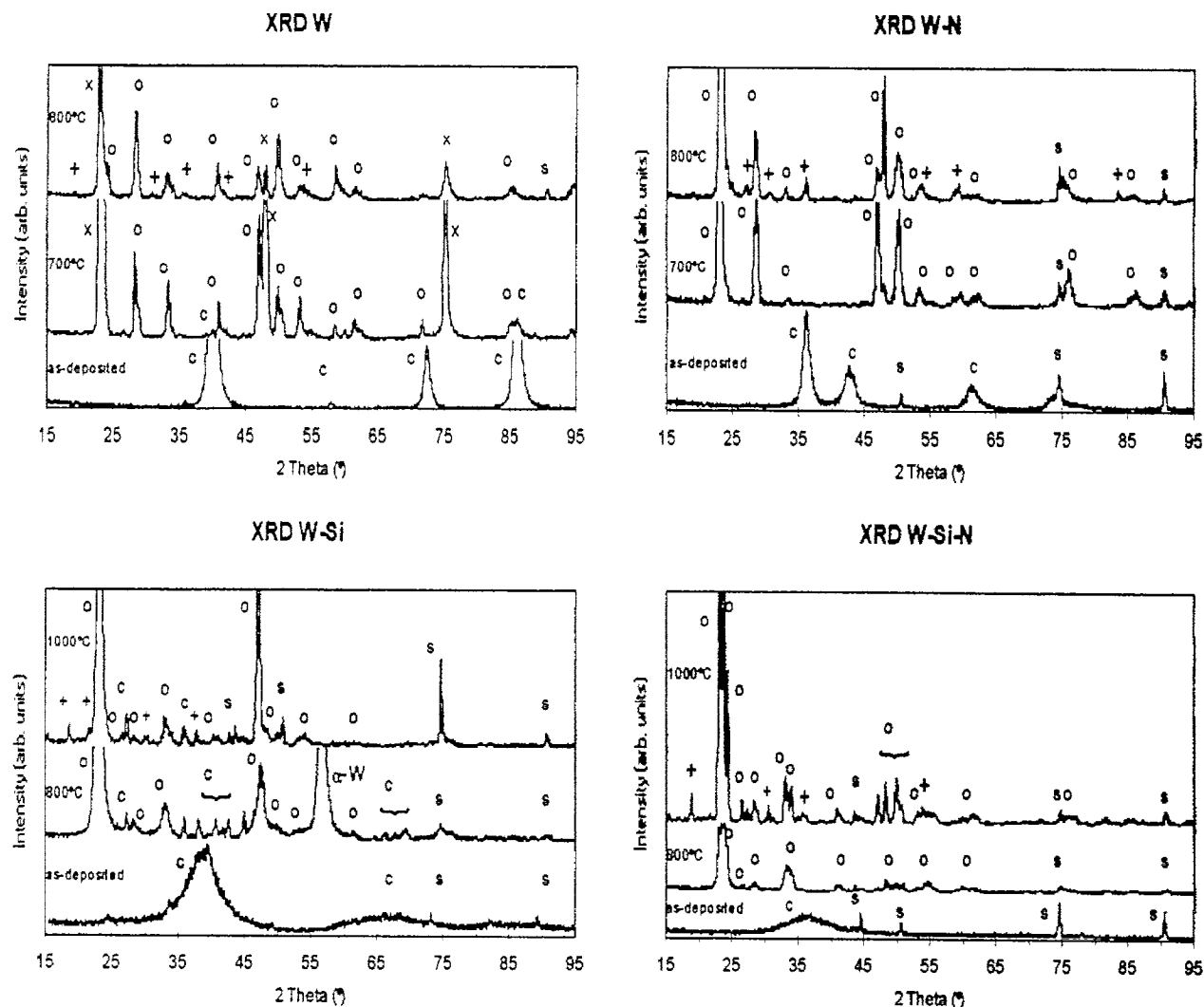


Fig. 3. Structural evolution of W (a), W-N (b), W-Si (c) and W-Si-N (d), with oxidation temperature; o, WO_3 ; x, WO_x ; +, FeWO_4 ; c, coating; s, substrate.

increasing temperatures up to 1000°C under a continuous flow of a gas mixture of $\text{Ar} + \text{H}_2$. X-ray diffractograms were taken at steps of 100°C in the range $[T_{\text{amb}}-600^\circ\text{C}]$, 50°C in the range $[600-900^\circ\text{C}]$ and 25°C in the range $[900-1000^\circ\text{C}]$.

A Cameca SX-50 electron probe microanalysis (EPMA) apparatus was used to determine the chemical composition of the coatings.

The cross-section of the films, its surface topology and morphological details were examined in a Jeol T330 scanning electron microscope (SEM). This apparatus was connected to an energy-dispersive X-ray detector (EDXS) (Tracor Instruments).

3. Results and discussion

3.1. As-deposited coatings

The chemical composition of the films was determined by

EPMA as W, $\text{W}_{45}\text{N}_{55}$, $\text{W}_{69}\text{Si}_{31}$ and $\text{W}_{24}\text{Si}_{21}\text{N}_{55}$. Concerning the Si content, as was observed for other W-N films, the presence of N makes the resputtering of the silicon during the deposition more difficult owing to the ion bombardment induced by the substrate bias. Consequently, a lower W/Si deposition rate is obtained for W-Si-N in comparison to W-Si films.

In agreement with the chemical composition, the films without Si present the b.c.c. α -W phase and the nitride phase, W_2N , for the films without and with nitrogen, respectively. However, in this last case, the nitride indexed does not correspond to the nitrogen content in the film, indicating that some free nitrogen should be present in excess in the nitride lattice.

Both films containing Si have mainly amorphous structures. However, in the film without N it is possible to observe signs of hexagonal WSi_2 superimposed on the broad amorphous diffraction peak. If the amorphism of the films should be expected taking into account literature results and the Si content of the films [3–5], the hexagonal

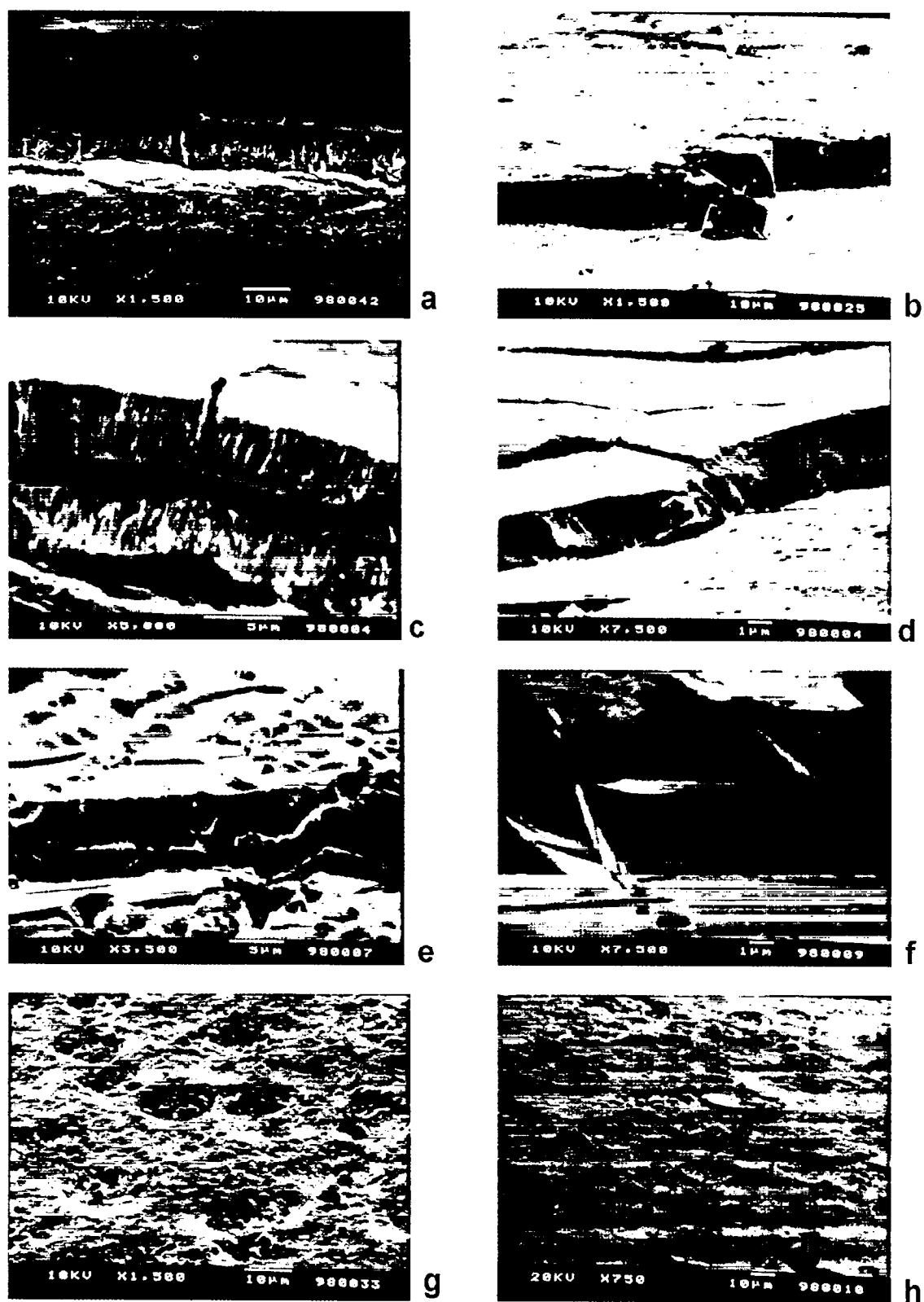


Fig. 4. SEM micrographs of the cross-section or surface morphologies of the oxide layers of: (a) W films oxidised at 750°C for 30 min, (b) W-Si film oxidised at 950°C for 30 min, (c) as-deposited W, (d) as-deposited W-N, (e) as-deposited W-Si, (f) as-deposited W-Si-N, (g) W-N film oxidised at 700°C for 30 min (h) W-Si-N film oxidised at 900°C for 30 min.

WSi₂ was not found, to our knowledge, in the literature. Moreover, this phase, although with the highest Si content of the W–Si phases, was detected in the film with a higher W/Si ratio, not being indexed for W–Si–N film. However, it is referred to in the literature [5,6] that the structure of W–Si materials depends on the processing conditions, it being possible to obtain WSi₂ in materials with low Si content [6].

In order to interpret the results of the oxidation at high temperatures it was necessary to study the thermal evolution of these amorphous films. Fig. 1 shows X-ray diffractograms for increasing annealing temperatures. In the case of W–Si film, crystallisation begins at 700°C with the formation of W₅Si₃ and α -W phases. This result is very close to that of Reid et al. [4] for similar chemical compositions. At 850°C, the transformation of pre-existing hexagonal into tetragonal WSi₂ was observed. This temperature is much higher than that of 600°C indicated in the work of LeGoues et al. [7], probably owing to their much higher silicon content (W/Si = 0.5).

The W–Si–N film does not suffer appreciable changes with increasing annealing temperatures up to 1000°C. The structure remains amorphous and only some changes in the position and form of the amorphous peak are observed. Up to 900°C there are small shifts in the peak position for low diffraction angles (due to the temperature increase), but for higher temperatures, there are important shifts in the inverse sense. Moreover, the peak narrows, probably indicating the beginning of crystallisation. Hirvonen et al. [2] found similar behaviour for Mo–Si–N films suggesting that these changes should be related to the relaxation and densification of the structure. They also detected a loss of nitrogen in the film towards the substrate. Our measurements by EPMA on the films after thermal annealing showed a 25% decrease of the initial N content and an increase in the W/Si value from 1.1 to 1.3, indicating that Si diffuses into the substrate. It should be remarked that this loss of Si was also observed for W–Si films; a W/Si value of 2.5 was found instead of the original 2.2.

3.2. Oxidation behaviour

Fig. 2 presents the isothermal mass change data for W–Si–N coated samples. In all the cases, the uncoated substrate behaviour for 1000°C is also shown. XRD diffractograms obtained from the oxidised films are presented in Fig. 3 for the different oxidation temperatures. Some important remarks can be made after a careful analysis of these figures:

- The oxidation resistance of the coatings containing Si is much higher than for W and W–N films, although no significant differences could be observed in the type of oxides detected by XRD. However, it should be pointed out that during the oxidation of silicides the protective scale is SiO₂ and this phase exists in the amorphous state for temperatures lower than 1000°C [8]. Thus, it

is probable that if a layer of SiO₂ exists it may not be detected by XRD. Another possible explanation is related to the density of the oxide layer. The oxide layers of the films containing Si are much more compact than those of the W and W–N films, as can be observed in Fig. 4a,b.

- This compact morphology should not be related to the as-deposited cross-section morphologies. In fact, excepting single W that presents a type 1 morphology following Thornton's classification, all the coatings, including W–N, are very dense (Fig. 4c–f).
- As would be expected, the oxidation behaviour of W is very similar to that obtained in previous work [1], whereas for W–N some changes can be observed, probably due to its higher N content. In this case, there is a severe cracking of the oxide layers during the test, particularly for temperatures higher than 700°C, leading to the fall off of some oxide particles from the sample holder and the sudden weight losses in the oxidation curves (Fig. 2). This is clearly shown in the picture presented in Fig. 4g. The N liberation during oxidation, in association to residual stresses in the as-deposited and oxide layers, promote oxide cracking. For higher temperatures, similar cracking is also observed for the W–Si–N films (Fig. 4h).
- For the highest oxidation temperatures the coatings with Si do not show the same total oxidation weight gains in spite of having the same as-deposited thickness. Moreover, the final stage of oxidation is not coincident with the substrate oxidation. This behaviour should be related to the inter-diffusion of elements (Si, Fe and N) between the film and the substrate. In consequence, when the oxidation reaches the substrate, this does not have the original composition, and, consequently, its oxidation behaviour should be different.
- The presence of crystallised phases in the W–Si film oxidation at 850°C should be noted, in agreement with the thermal annealing results presented above.

4. Conclusions

The introduction of Si in W–N sputtered films leads to amorphous structures.

- W₂₄Si₂₁N₅₅ films keeps an amorphous structure up to 1000°C whereas W₆₉Si₃₁ crystallises at 750°C as α -W and W₅Si₃.
- Si-containing films have better oxidation resistance than W and W–N coatings which is promising for applications where the service temperature is higher than 800°C.

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